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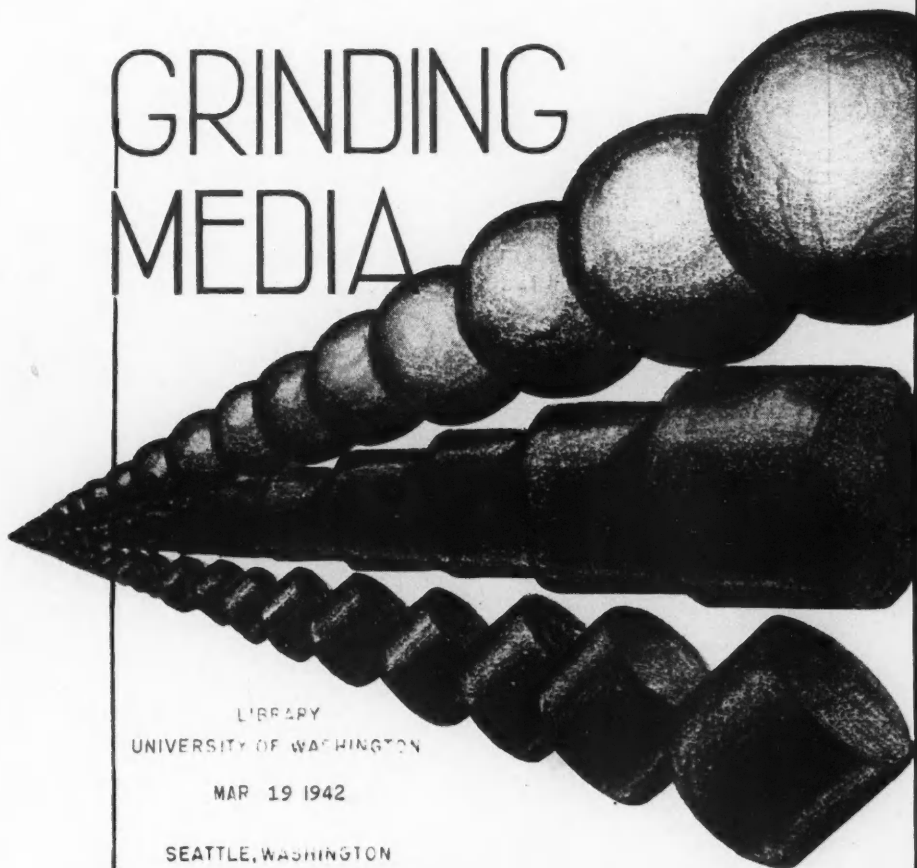
CEMENT AND LIME MANUFACTURE

VOL. XV. No. 2

FEBRUARY 1942

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The Sulphate Resistance of Portland Cements.

THE following is an abstract of research paper RP1411 of the U.S. National Bureau of Standards, by Messrs. E. P. Flint and L. S. Wells. The paper shows that isometric $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, a constituent of set Portland cement, is readily converted by sodium sulphate solutions to $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31.5\text{H}_2\text{O}$. Partial replacement of the Al_2O_3 in $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ by Fe_2O_3 or of the H_2O by SiO_2 gives "hydrogarnets" which are stable in the presence of sulphate solutions. Such substitutions may be brought about by inducing reactions between tricalcium aluminate hydrate and silica from various sources in the set cement or from added pozzolanic materials, and by increasing the content of glass and tetracalcium aluminoferrite in the cement. Products having an X-ray structure nearly identical with that of grossularite garnet result when properly proportioned mixtures, made up of the pozzolanic material, dehydrated kaolin, with tricalcium silicate, or with lime and beta dicalcium silicate, are steamed at 500 deg. C. and 420 atmospheres.

The authors point out that various investigators¹ have demonstrated the existence of a general correlation between the potential tricalcium aluminate content of Portland cements of low glass content and the resistance to sulphate action of mortars and concretes made from these cements. The typical reaction which occurs during sulphate disintegration involves conversion of the hydration products of tricalcium aluminate to gypsum and the "high-sulphate form" of calcium sulphoaluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31.5\text{H}_2\text{O}$. This transformation is accompanied by considerable expansion which eventually may disrupt the specimen.

There are a number of methods by which the sulphate resistance of Portland cement mortar or concrete can be increased, including (1) Steaming the mortar or concrete², (2) Prolonged curing of the mortar or concrete at ordinary temperatures³, (3) Mixing the cement with a pozzolanic material⁴, (4) Increasing the

glass content of the cement⁵, (5) Altering the chemical composition of the cement³.

In view of the relationship between the tricalcium aluminate content and disintegration tendency of the cement, it seemed probable that these methods might be efficacious in the degree to which they convert the aluminate content of the set cement into a form not readily attacked by sulphate solutions. Recent work⁶ suggested that this stabilised aluminate might consist of silica- or iron-containing hydrogarnet. Experiments which support this hypothesis are reported in this paper.

Resistance of Hydrogarnets to Sodium Sulphate Solution.

Samples of hydrogarnet preparations having compositions shown in Fig. 1 were available from a previous study. The isometric tricalcium aluminate

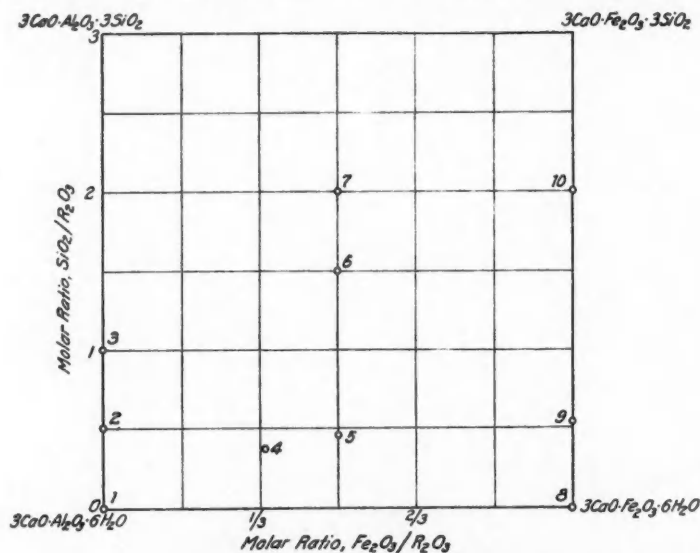


Fig. 1. Compositions of Garnet-Hydrogarnet Limes Exposed to Sodium Sulphate Solution.

hexahydrate (1, Fig. 1), prepared by treating anhydrous tricalcium aluminate with steam at 150 deg. C. in an autoclave, was practically free from silica and ferric oxide. The tricalcium ferrite hexahydrate (8, Fig. 1) was obtained by reaction of ferric chloride solution with boiling limewater. This preparation contained a certain amount of silica, probably combined as hydrated calcium silicate, since a determination of the unit cell size of the sample gave practically the theoretical value for $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$.

A sulphate test solution was desired which would contain a sufficient concentration of calcium ions to prevent undue hydrolysis of the hydrogarnet preparations placed in contact with it. Such a solution was prepared by mixing

100 g. of anhydrous sodium sulphate with 1 litre of saturated lime solution (1.15 g. of CaO per litre). The resulting mixture was slightly supersaturated with respect to gypsum, and some precipitation of this compound occurred. To 100-ml. quantities of the test solution, in tightly-stoppered flasks, 0.5-g. samples of the hydrogarnet preparations were added. The flasks were allowed to stand with occasional daily shaking. Small samples of the solid phases were filtered off at intervals and examined microscopically.

Transformation of the $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ to well-developed needles of the "high-sulphate form" of sulphoaluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31.5\text{H}_2\text{O}$, began within a few hours and was complete after two days' contact with the sulphate solution. The sulphoaluminate was unchanged by standing six months longer in contact with the solution.

The aluminate preparation containing no ferric oxide and only 7.7 per cent. of silica (2, *Fig. 1*) was not perceptibly altered until after about four months, when a very small amount of finely-divided material having the mean refractive index of the sulphoaluminate appeared. This product increased to about 10 per cent. of the sample in six months. Preparations 4 and 5 (*Fig. 1*), which had $\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$ molar ratios of 2 : 1 (12.8 per cent. of Fe_2O_3) and 1 : 1 (18.4 per cent. of Fe_2O_3) and contained the lowest amounts of silica, showed a small amount of apparently amorphous material surrounding the isometric crystals after six months' contact with the sulphate solution. No appreciable alteration of any of the other preparations tested was observed during the six-months' period.

Thus the hydrogarnets which contain 10 to 15 per cent. or more of either silica or ferric oxide appear to be very resistant to transformation by the sulphate test solution. It can be postulated, therefore, that the sulphate resistance of set Portland cements, will be greatly improved if the aluminate compounds which they contain are converted to silica- or iron-containing hydrogarnets.

Effect of Hydrothermal Treatment of Mixtures of Aluminates and Silicates.

Mixtures of isometric $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ with definite amounts of various hydrated calcium silicates were prepared for treatment with water over a range of temperatures. A few mixtures of anhydrous tricalcium aluminate and the anhydrous calcium silicates were also included. The synthesis of the hydrated calcium silicates has been described in an earlier publication.⁷

Some of the mixtures were placed in saturated lime solution (0.5 g. of mixture in 200 ml. of solution) at ordinary temperatures; the remainder were placed in high-pressure autoclaves and heated with sufficient water to ensure the presence of liquid at the temperatures used. At the completion of the heating period samples of the solid phase were withdrawn, washed with alcohol and ether, and examined microscopically. From the relationship between index of refraction and composition in the $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ - $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ solid-solution series, given in *Fig. 2*, the approximate composition of the isometric phase could be estimated from a determination of its refractive index. *Fig. 2* was constructed

from index of refraction values reported in the literature for $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, plazolite, and grossularite, and from values for two synthetic preparations obtained in this study.

Owing to the very different rates of reaction with water of the aluminate and silicate compounds in cement, it is probable that tricalcium aluminate hexahydrate will occur in set cement associated with hydrated calcium silicates of different compositions and stages of crystallisation. However, if such products are unstable with respect to hydrated calcium aluminosilicates, further reactions

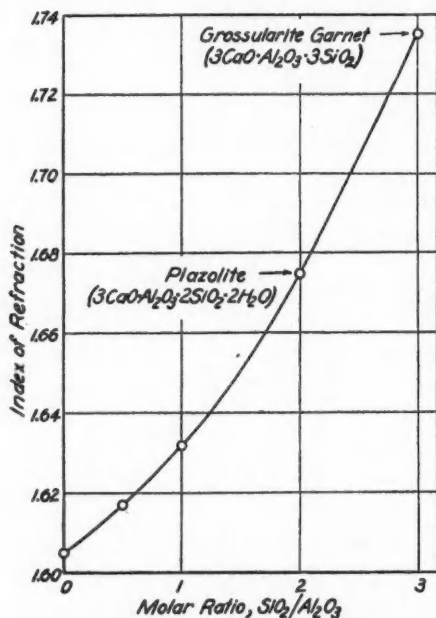
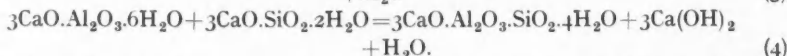
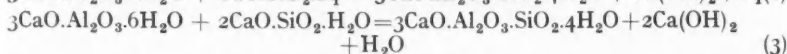
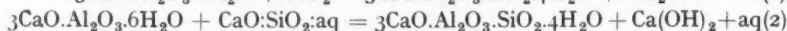
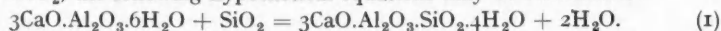


Fig. 2. Relationship between Index of Refraction and Composition in the Solid Solution Series $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} - 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$.

may occur. Restricting consideration to mixtures having the molar ratio $1\text{Al}_2\text{O}_3 : 1\text{SiO}_2$, the following hypothetical equations may be formulated:



According to Fig. 2, the index of refraction of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 4\text{H}_2\text{O}$ is approximately 1.63. Therefore, if the reactions proceed to completion, the products will consist entirely of calcium hydroxide and an isometric phase of

TABLE I.—FORMATION OF SILICA-CONTAINING HYDROGARNETS FROM MIXTURES OF ALUMINATES AND SILICATES.

Experiment number	Compounds mixed	Molar ratio $\text{Al}_2\text{O}_3/\text{SiO}_2$ in mixture	Temperature °C	Pressure Atmospheres	Time Days	Index of refraction of refractive phase in product	Other phases in product
1	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + \text{SiO}_2$ gel	1:1	25	1	92	1.605	Amorphous, low-index material.
2	do.	1:1	250	5	7	1.62	Do.
3	do.	1:1	250	33	18	1.62 to 1.64	Do.
4	do.	1:1	350	163	10	1.67	Do.
5	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + \text{CaO} \cdot \text{SiO}_2$ eq 1	1:2	25	1	64	1.605 to 1.61	Amorphous, low-index material.
6	do.	1:1	25	5	7	1.625 to 1.635	$\text{Ca}(\text{OH})_2$.
7	do.	1:1	150	5	21	1.625 to 1.635	Do.
8	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + 2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}^*$	1:1	250	39	34	1.63	Do.
9	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + 10\text{CaO} \cdot \text{SiO}_2 \cdot 6\text{H}_2\text{O}^*$	1:1	250	39	34	1.62 to 1.625	$10\text{CaO} \cdot \text{SiO}_2 \cdot 6\text{H}_2\text{O} + \text{Ca}(\text{OH})_2$.
10	do.	1:1	25	5	31	1.62 to 1.625	Do.
11	do.	1:1	150	39	62	1.62 to 1.63	$\text{Ca}(\text{OH})_2$.
12	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + 3\text{CaO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$	1:1	25	5	32	1.61 to 1.62	$3\text{CaO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} + \text{Ca}(\text{OH})_2$.
13	do.	1:1	150	5	32	1.62 to 1.625	Do.
14	do.	1:1	250	39	10	1.62 to 1.63	Do.
15	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 2\text{CaO} \cdot \text{SiO}_2$	1:1	200	15	12	1.62 to 1.63	$10\text{CaO} \cdot \text{SiO}_2 \cdot 6\text{H}_2\text{O} + \text{Ca}(\text{OH})_2$.
16	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3\text{CaO} \cdot \text{SiO}_2$	2:1	200	15	11	1.62	Do.
17	do.	1:1	200	15	5	1.62 to 1.63	Do.
18	do.	1:2	350	163	5	1.62 to 1.63	$3\text{CaO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} + \text{Ca}(\text{OH})_2$.

* Amorphous hydrated monocalcium silicate.

* Needle-form of dicalcium silicate hydrate, mean index of refraction 1.60 (see reference [7]).

* Orthorhombic dicalcium silicate hydrate, $\alpha=1.614$, $\beta=1.620$, $\gamma=1.633$ (see reference [7]).

index 1.63. Table I shows that this condition is very nearly fulfilled in experiments Nos. 3, 6, 7, 8 and 11, where sufficient time had been allowed at the temperatures given for complete transformation of the original materials. In most cases the index of refraction of the isometric phase was not uniform but showed a variation of about 0.01 unit. This variation is probably caused by imperfect mixing of the original samples and by difficulty in obtaining uniform reaction between crystals of low solubility. In experiment No. 3, a rise in index of refraction of the isometric crystals to as much as 1.64 may have been caused by a concentration of silica in the outer portion of the crystals. Numerous crystals having the higher indexes of refraction contained cores of lower index.

A mixture of tricalcium aluminate hexahydrate and silica gel in the molar proportion $1\text{Al}_2\text{O}_3 : 2\text{SiO}_2$, treated with water at 350 deg. C. for 10 days, was completely converted to an isometric phase having an index of refraction approximately that of plazolite $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ (experiment No. 4).

Mixtures of anhydrous tricalcium aluminate with beta-dicalcium and tricalcium silicates (experiments Nos. 15 to 18) gave reaction products similar to those of the hydrated compounds. The isometric phase in these preparations was formed in an extremely finely divided state. Variation of the ratio of aluminate to silicate had little effect on the index of refraction of the isometric product. With an excess of silicate present the temperature and duration of the experiment are the factors which determine the extent of substitution of silica in the isometric hydrated aluminate.

At room temperature, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ reacts with hydrated dicalcium silicate (experiment No. 9) and hydrated tricalcium silicate (experiment No. 12) to form silica-containing hydrogarnets, whereas with silica gel (experiment No. 1) or amorphous hydrated monocalcium silicate (experiment No. 5), there is little evidence of such a reaction. It is possible that the amorphous reaction products in these experiments may form a layer of low permeability on the crystals of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, thereby diminishing the rate of diffusion of silica into the aluminate.

Steam curing is one of the most effective means of increasing the sulphate resistance of Portland cement mortars and concretes. These experiments show that the essential change produced by steam curing appears to be the removal from the set cement of tricalcium aluminate hexahydrate, which is unstable in the presence of sulphate solutions, and the formation of a silica-containing hydrogarnet, which is stable in such solutions. The crystallisation of hydrated calcium silicates and reduction in free calcium hydroxide, which accompany steam treatment, are probably factors of less importance. In curing at ordinary temperatures the formation of silica-containing hydrogarnets may likewise be the determining factor. Both the rate of conversion of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ and the improvement in sulphate resistance at such temperatures are very slow.

Effect of Hydrothermal Reactions of Cement Compounds with Burnt-Clay Pozzolana.

Dehydrated Georgia kaolin was selected as a typical burnt-clay pozzolana. The original material, before ignition, had the following composition: SiO_2 ,

45.94 per cent.; Al_2O_3 , 38.22 per cent.; Fe_2O_3 , 0.45 per cent.; TiO_2 (+ ZrO_2 , etc.), 1.34 per cent.; Ignition loss, 13.39 per cent. The kaolin was dehydrated by heating for two hours at 700 deg. C. Mixtures of this material with various cement compounds were then prepared and treated with water at elevated temperatures and pressures. Microscopical examinations were made of the resulting products. In two experiments the dehydrated kaolin was replaced by a coprecipitated alumina-silica gel having a molar ratio of $1\text{Al}_2\text{O}_3 : 2\text{SiO}_2$.

Hypothetical reactions of dehydrated kaolin with the various cement compounds in the presence of water may be represented by the following equations:

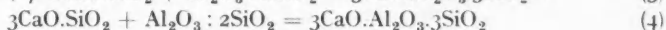
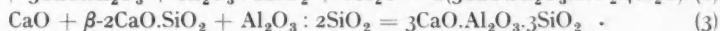
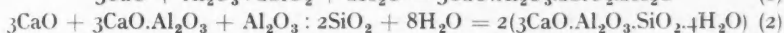
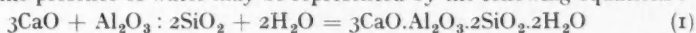


TABLE II.—FORMATION OF SILICA-CONTAINING HYDROGARNETS FROM MIXTURES OF CEMENT COMPOUNDS AND DEHYDRATED KAOLIN.

Experiment number	Molar ratio of mixture	Temperature	Pressure	Time	Index of refraction of isometric phase in product		Approximate amount of isometric phase in product
					Observed	Theoretical (assuming complete reaction)	
19	$3\text{CaO} : \text{Al}_2\text{O}_3 : 2\text{SiO}_2$	°C	atm	Days			Percent
20	do.....	150	5	14	1.64 to 1.65	1.675	70 to 80
21	do.....	350	163	11	1.65 to 1.66	1.675	80 to 90
22	do.....	350	163	11	1.64	1.675	50
23	$3\text{CaO} : 3\text{CaO} \cdot \text{Al}_2\text{O}_3 : \text{Al}_2\text{O}_3 : 2\text{SiO}_2$	225	25	14	1.625 to 1.63	1.63	90
24	$\text{CaO} : 2\text{CaO} \cdot \text{SiO}_2 : \text{Al}_2\text{O}_3 : 2\text{SiO}_2$	500	420	27	1.72	1.735	90
25	$3\text{CaO} \cdot \text{SiO}_2 : \text{Al}_2\text{O}_3 : 2\text{SiO}_2$	250	39	30	1.65	1.735	50
26	do.....	500	420	7	1.70	1.735	80

Table II permits a comparison of the observed values for the index of refraction of the isometric phase with the theoretical index which would result from complete combination of the cement compound with the aluminium silicate. The values obtained in experiments Nos. 20, 22, 23, and 25 indicate that reactions 1, 2, 3, and 4, respectively, proceed almost to completion at the temperatures and with the reaction periods chosen.

Dehydrated kaolin was replaced by coprecipitated alumina-silica gel in experiment No. 21. Less of the isometric product was formed and it was poorly crystallised compared with that of experiment No. 20. In a repetition of experiment No. 21, the coprecipitated gel was dehydrated at 700 deg. prior to mixing with lime. The product of hydrothermal treatment in this case was somewhat better crystallised than that obtained from the undehydrated gel but the difference was not particularly marked.

Well-crystallised preparations were obtained by steaming mixtures of beta-dicalcium silicate, lime, and dehydrated kaolin and of tricalcium silicate and dehydrated kaolin at 500 deg. C. and 420 atmospheres. The product of experiment No. 23, particularly, gave an X-ray pattern which showed practically

no shift in lines from the pattern of grossularite garnet. The much slower rate of combination of dehydrated kaolin with tricalcium silicate at 250 deg. C. than at 500 deg. C. is illustrated by experiments Nos. 24 and 25.

These results cannot be applied directly to an explanation of the high sulphate resistance of Portland-pozzolana cements because mortars and concretes made from such cements are usually not subjected to steam curing. Also the initial products of reaction of dehydrated kaolin with lime in the presence of water at ordinary temperatures are different from the isometric crystals obtained at elevated temperatures. As reported by Strätling⁸ and confirmed in unpublished work in this laboratory, the products at room temperature occur as hexagonal plates which are similar in appearance to the hexagonal forms of the hydrated calcium aluminates. These plate-like crystals belong to a series of hydrated calcium silicoaluminates which appear to bear a close relationship to the calcium aluminate complex salts.

A sample of one of the hexagonal silicoaluminate preparations, exposed to the sulphate test solution, was about 50 per cent. converted to the sulphoaluminate in 10 days. After three weeks practically no hexagonal crystals remained. The hexagonal silicoaluminates therefore appear to be much less resistant than the isometric calcium aluminosilicates (hydrogarnets) to transformation by the sulphate solution. This same experiment, however, indicates that the hexagonal compounds probably possess a higher solubility than the hydrogarnets and, if initially protected from sulphate action, should be gradually transformed to the hydrogarnets at ordinary temperatures. Such alteration would lead to increased sulphate resistance of the Portland-pozzolana mortar.

Effect of Increase in Glass Content.

In a previous paper⁶, it was shown that glasses, representative of the compositions of various liquid phases formed in Portland cement clinker at 1,400 deg. C., will react with water at elevated temperatures to give hydrogarnets containing iron and silica. In order to ascertain whether or not similar reactions will occur at ordinary temperatures, powdered samples of three of the glasses used in the former study were made into pastes with 50 per cent. of their weight of water and stored in sealed phials. The three glasses had the following compositions:

	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂
	Per cent.	Per cent.	Per cent.	Per cent.
Glass A	58.3	33.0	0.0	8.7
Glass B	56.7	30.3	5.0	8.0
Glass C	54.8	22.7	16.5	6.0

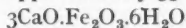
After two months' storage, about 50 per cent. of glasses A and B had been converted to isometric crystals having indexes of refraction of 1.62 and 1.62 to 1.63, respectively, and about 10 per cent. of glass C had altered to isometric crystals having a refractive index of 1.64 to 1.65. No separation of hematite or formation of hexagonal calcium aluminate hydrate was observed.

Increase of the glass content of Portland cement clinker occurs partly at the expense of crystalline tricalcium aluminate, which is very susceptible to sulphate attack. Thus, reducing the content of tricalcium aluminate and increasing that of the glass, which will hydrate to silica- and iron-containing hydrogarnet, would be expected to improve the sulphate resistance of Portland cement. Such improvement, with increase in glass content of cements, has been reported by Parker⁵.

Effect of Increasing Alumina-Ferric Oxide Ratio.

Cements having a low alumina-ferric oxide ratio are considerably more resistant to sulphate action than those having a high ratio. Compositions of the former type are relatively high in potential tetracalcium aluminoferrite and low in potential tricalcium aluminate, whereas the reverse situation obtains in the latter type.

The much greater sulphate resistance of tetracalcium aluminoferrite than of tricalcium aluminate is explained by the fact, established in a previous study⁶, that, when mixed with sufficient water to form a paste, the ferrite hydrates to give an iron-containing hydrogarnet while the aluminate hydrates to iron-free calcium aluminate hydrate. The unit cell size of the isometric phase obtained from a paste of tetracalcium aluminoferrite at room temperature was 12.60 Å (angstroms), or 0.04 Å higher than that of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. The unit cube size of $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ is 12.74 Å, or 0.18 Å higher than that of the aluminate. Since a linear relationship exists between unit cube size and composition expressed in moles per cent. in the series $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ - $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, a unit cube size of 12.60 Å would correspond approximately to a solid solution containing $0.04/0.18 \times 100 = 22$ moles per cent. of $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ in 78 moles per cent. of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. A sample of tetracalcium aluminoferrite steamed at 225 deg. C. gave an isometric product having a unit cube size of 12.62 Å, corresponding to a solid solution of approximately 33 moles per cent. of



in 67 moles per cent. of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. Both of these solid solutions would be rather resistant to sulphate action.

Summary.

Experiments on the constituents, and on the possible hydration products, of Portland cement indicate that the sulphate resistance of Portland cement should be increased by any method resulting in the removal from the set cement of tricalcium aluminate hexahydrate, which is unstable in sulphate solutions, and substitution for the aluminate of hydrogarnets containing iron or silica, which are stable in such solutions. Such substitution may be brought about by (1) reaction of the hydrated aluminate with silica from the various silicates in the set cement, (2) addition of a pozzolanic material to the cement, and (3) increasing the glass and tetracalcium aluminoferrite contents of the cement. Additional studies will be necessary to determine to what extent the members of the hydrogarnet solid-solution series are actually formed, or can be made to form in the setting and hardening of various cements and cement-pozzolana mixtures at ordinary temperatures. Preparations having an X-ray structure nearly identical

with that of grossularite garnet resulted when mixtures of beta-dicalcium silicate, lime, and dehydrated kaolin, and also of tricalcium silicate and dehydrate kaolin, were steamed at 500 deg. C. and 420 atmospheres.

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The Density of Cement Slurry.

A NEW method of ascertaining the density of slurry in wet-process cement plants is described by Mr. W. R. Bendy, of New York, in a recent number of "Pit and Quarry," from which the following is taken.

One hundred grammes of slurry containing 40 per cent. moisture is made up of 40 gr. of water and 60 gr. of raw material. At 30 deg. C. water weighs 0.9957 gr. per c.c. If the dry raw material weighs 2.7 gr. per c.c., the density of the slurry may be calculated as follows:

60 gr. of raw material at 2.7 gr. per c.c. occupies a volume of $\frac{60}{2.700} = 22.22$ c.c.

40 gr. of water weighing 0.9957 gr. per c.c. occupies a volume of $\frac{40}{0.9957} = 40.71$ c.c.

100 gr. of slurry occupies a total volume of 62.39 c.c.

$\frac{60}{62.39} = 0.962$ gr. of solids per c.c. of slurry.

$\frac{40}{62.39} = 0.641$ gr. of water per c.c. of slurry.

$\frac{100}{62.39} = 1.603$ gr. total weight per c.c. of slurry.

The same calculations may be made in general terms: P = Percentage of moisture in slurry; R = density of raw material in gr. per c.c.; d = density of water in gr. per c.c.:

$$\text{Grammes of raw material per c.c. of slurry} = \frac{1}{\frac{P}{d(100-P)} + \frac{1}{R}}$$

$$\text{Grammes of water per c.c. of slurry} = \frac{1}{\frac{(100-P)}{PR} + \frac{1}{d}}$$

$$\text{Total weight of slurry, grammes per c.c.} = \frac{100}{\frac{(100-P)}{R} + \frac{P}{d}}$$

Methods of determining the density or specific gravity of solids usually involve the use of a liquid in which the solid neither dissolves nor reacts. In this case, however, we are interested only in the apparent density in water, which value may be affected by the solution of small quantities of the solids and also by drying and subsequent rewetting. Methods which involve drying as a preliminary step may give a figure as much as $\frac{1}{2}$ per cent. lower than the apparent value in actual slurry. Therefore it is preferable to make the determination on wet slurry without drying.

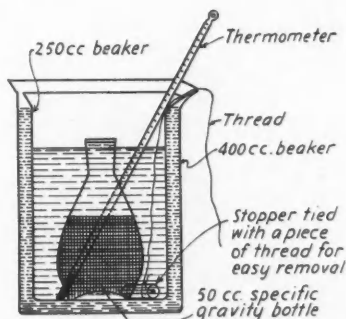


Fig. 1. Apparatus for the Determination of the Density of Slurry.

For accurate work with a gritty material like slurry the use of an ordinary specific-gravity bottle or pycnometer presents difficulties. These may be avoided by the following method, for which the only special apparatus necessary is an unadjusted specific-gravity bottle of 50 c.c. capacity. The specific-gravity bottle is weighed under four conditions: (1) Dry and empty, (2) full of distilled water, (3) partly filled with slurry, and (4) completely filled with water on top of the slurry weighed in (3). In addition, the percentage of moisture in the slurry must be determined separately, and the density of the water at the temperature of the test must be known. Care must be taken to have the bottle, the contents, and the stopper at exactly the standard temperature when the stopper is inserted. To obtain a stable and exact temperature, a double water bath is used as shown in Fig. 1.

The beakers are partly filled with water at approximately the standard temperature and are placed one inside the other. The temperature of the water in the inner beaker is then adjusted by gently warming or cooling the outer beaker; it should be held within 0.1 deg. C. of the standard temperature for at least fifteen minutes to allow the bottle and contents to attain a steady temperature. The stopper is then removed from the beaker and quickly inserted in the mouth of the bottle. Excess water is wiped off the end of the capillary opening in the stopper before the bottle is removed from the bath. Then the bottle is removed, dried on the outside, and weighed. When the bottle is removed from the bath,

slight temperature changes sometimes cause a bead of water to be forced out of the capillary. This should not be wiped off. At other times the level may fall in the capillary. In neither case is there any error provided the capillary opening in the stopper is level full while the bottle is still in the constant-temperature bath. Slurry may be placed in the bottle with a pipette so as to leave the inside of the neck perfectly clean; it is usually convenient to fill the bottle about three-quarters full of slurry. After weighing the bottle is filled with distilled water, which is dropped slowly down the side to avoid agitating the slurry. Then the temperature is adjusted exactly and the stopper is inserted as described.

If the slurry is thick enough to contain air bubbles the procedure should be varied slightly. The bottle is filled only about half full of slurry, and water is added until it is about three-quarters full. The forefinger is placed over the opening and the mixture thoroughly shaken to dilute the slurry and to allow the escape of bubbles of entrapped air. The mixture is then allowed to settle, and any particles of slurry adhering to the inside of the neck are carefully washed down. Finally the bottle is completely filled with distilled water, which is added carefully so that only clear water remains at the top and the final closing of the stopper is not impeded by gritty particles.

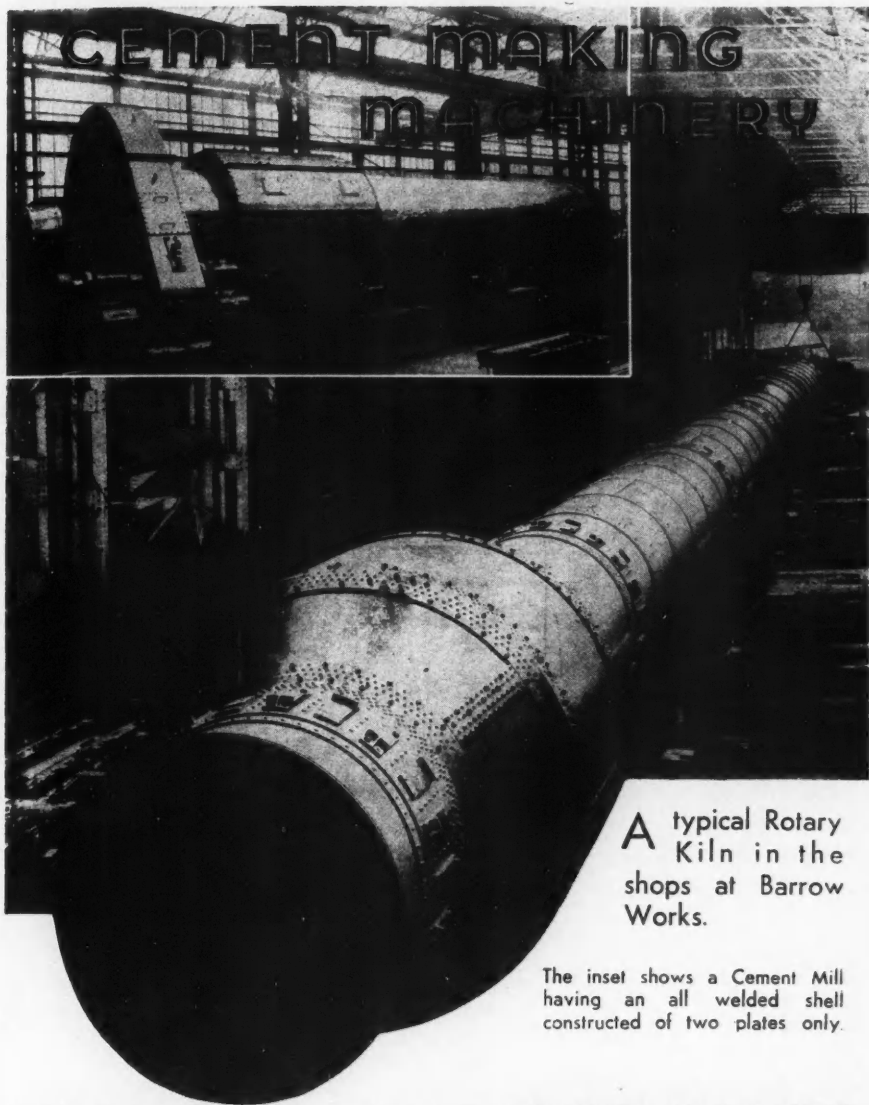
Calculations are based on the apparent density of the "dry" raw material. For many raw materials it is difficult to define exactly the condition "dry." Therefore, in determining the moisture content of the original slurry sample the ordinary control procedure should be used instead of more refined methods of drying, such as double drying, pulverizing before the final drying, or cooling in a desiccator, which are not usually followed in ordinary control work. The slurry-moisture records at most plants are the averages of the routine control determinations, and are used in all calculations. If, in determining dry raw-material density, the moisture is determined by the regular method, the final results in terms of slurry density will be correct even though the moisture content may be slightly in error.

The calculation of the density of the dry raw material is made as follows. P = Percentage of moisture in slurry; d = density of water at temperature of determination; B = weight of empty bottle (carefully dried); W = weight of bottle full of water; S = weight of bottle partly filled with slurry; T = weight of bottle containing slurry and filled with water.

$$\text{Density of dry raw material} = \frac{d}{1 - \frac{(T - W)}{(S - B) \left(1 - \frac{P}{100}\right)}} \text{ gr. per c.c.}$$

Example.—

Temperature	30 deg. C.
Weight of empty bottle	$B = 17.6455 \text{ gr.}$
Weight of bottle full of water	$W = 67.0957 \text{ gr.}$
Weight of bottle partly filled with slurry	$S = 73.4633 \text{ gr.}$
Weight of bottle, slurry and water	$T = 90.3442 \text{ gr.}$
Slurry moisture	$P = 34.18 \text{ per cent.}$



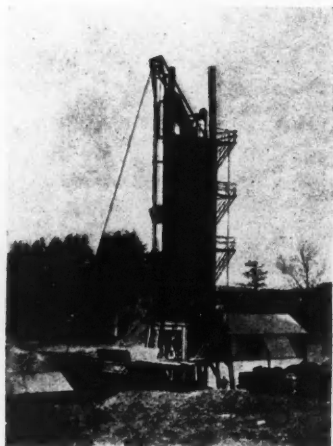
A typical Rotary Kiln in the shops at Barrow Works.

The inset shows a Cement Mill having an all welded shell constructed of two plates only.

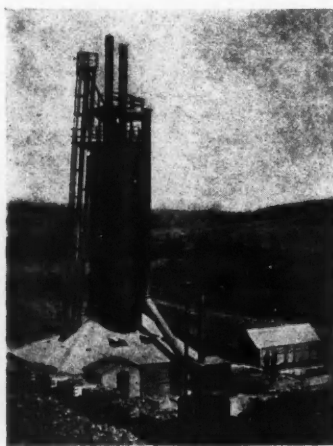
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TABLE I.—COMPONENT WEIGHTS OF SLURRY.
(Grammes per cubic centimetre of Slurry at 30 deg. C.)
(See Table II for multiplying factors.)

Moisture in Slurry (%)		Density of Dry Raw Material (grams per cc.)									
		2.70	2.71	2.72	2.73	2.74	2.75	2.76	2.77	2.78	2.79
30	Dry Material Water Slurry	1.249 0.535 1.784	1.251 0.536 1.787	1.253 0.537 1.790	1.255 0.538 1.793	1.257 0.539 1.796	1.259 0.540 1.799	1.261 0.541 1.802	1.264 0.541 1.805	1.266 0.542 1.808	1.268 0.543 1.811
		1.217 0.547 1.764	1.219 0.548 1.767	1.221 0.549 1.770	1.223 0.550 1.773	1.225 0.551 1.776	1.227 0.552 1.779	1.229 0.552 1.781	1.231 0.553 1.784	1.233 0.554 1.787	1.235 0.555 1.790
		1.186 0.558 1.744	1.188 0.559 1.747	1.190 0.560 1.750	1.192 0.561 1.753	1.194 0.562 1.756	1.196 0.563 1.759	1.197 0.563 1.761	1.199 0.565 1.764	1.201 0.566 1.767	1.203 0.567 1.770
31	Dry Material Water Slurry	1.156 0.569 1.725	1.158 0.570 1.728	1.160 0.571 1.731	1.161 0.572 1.733	1.163 0.573 1.736	1.165 0.574 1.739	1.167 0.575 1.742	1.169 0.575 1.744	1.170 0.577 1.747	1.172 0.578 1.750
		1.126 0.581 1.707	1.128 0.581 1.709	1.130 0.582 1.712	1.132 0.583 1.715	1.133 0.584 1.717	1.135 0.585 1.720	1.137 0.585 1.722	1.138 0.587 1.725	1.140 0.587 1.727	1.142 0.588 1.730
		1.098 0.591 1.689	1.099 0.592 1.691	1.101 0.593 1.694	1.102 0.594 1.696	1.104 0.595 1.699	1.106 0.595 1.701	1.107 0.596 1.703	1.109 0.597 1.706	1.110 0.598 1.708	1.112 0.599 1.711
32	Dry Material Water Slurry	1.069 0.602 1.671	1.071 0.602 1.673	1.072 0.603 1.675	1.074 0.604 1.678	1.075 0.605 1.680	1.077 0.606 1.683	1.078 0.607 1.685	1.080 0.608 1.688	1.081 0.609 1.690	1.083 0.609 1.692
		1.041 0.612 1.653	1.043 0.612 1.655	1.044 0.614 1.658	1.046 0.614 1.660	1.047 0.615 1.662	1.049 0.616 1.665	1.050 0.617 1.667	1.052 0.617 1.669	1.053 0.619 1.672	1.055 0.619 1.674
		1.014 0.622 1.636	1.016 0.622 1.638	1.017 0.623 1.640	1.018 0.624 1.642	1.020 0.625 1.645	1.021 0.626 1.647	1.023 0.627 1.650	1.024 0.628 1.652	1.025 0.629 1.654	1.027 0.629 1.656
33	Dry Material Water Slurry	0.988 0.631 1.619	0.989 0.632 1.621	0.990 0.633 1.623	0.992 0.634 1.626	0.993 0.635 1.628	0.994 0.636 1.630	0.996 0.636 1.632	0.997 0.637 1.634	0.998 0.638 1.636	0.999 0.639 1.638
		0.962 0.641 1.603	0.963 0.642 1.605	0.964 0.643 1.607	0.965 0.644 1.609	0.967 0.645 1.611	0.968 0.645 1.613	0.969 0.646 1.615	0.970 0.647 1.617	0.972 0.648 1.619	0.973 0.648 1.621
		0.936 0.651 1.587	0.937 0.652 1.589	0.938 0.653 1.591	0.940 0.653 1.593	0.941 0.654 1.595	0.942 0.655 1.597	0.943 0.656 1.599	0.944 0.657 1.601	0.945 0.657 1.602	0.947 0.657 1.604
34	Dry Material Water Slurry	0.911 0.660 1.571	0.912 0.661 1.573	0.913 0.662 1.575	0.914 0.663 1.577	0.916 0.663 1.579	0.917 0.664 1.580	0.918 0.664 1.582	0.919 0.665 1.584	0.920 0.666 1.586	0.921 0.667 1.588
		0.887 0.668 1.555	0.888 0.669 1.557	0.889 0.670 1.559	0.890 0.671 1.561	0.891 0.672 1.563	0.892 0.673 1.565	0.893 0.673 1.566	0.894 0.674 1.568	0.895 0.675 1.570	0.896 0.676 1.572
		0.862 0.678 1.540	0.863 0.679 1.542	0.864 0.680 1.544	0.865 0.681 1.546	0.866 0.681 1.547	0.867 0.682 1.549	0.868 0.683 1.551	0.869 0.684 1.553	0.870 0.684 1.554	0.871 0.685 1.556
35	Dry Material Water Slurry	0.839 0.686 1.525	0.840 0.687 1.527	0.841 0.688 1.529	0.842 0.688 1.530	0.843 0.689 1.532	0.844 0.690 1.534	0.845 0.691 1.536	0.845 0.692 1.537	0.846 0.693 1.539	0.847 0.694 1.541
		0.816 0.695 1.511	0.817 0.695 1.512	0.818 0.696 1.514	0.818 0.697 1.515	0.819 0.698 1.517	0.820 0.699 1.519	0.821 0.700 1.521	0.822 0.700 1.522	0.823 0.701 1.524	0.824 0.701 1.525
		0.793 0.703 1.496	0.794 0.704 1.498	0.795 0.704 1.499	0.796 0.705 1.501	0.797 0.706 1.503	0.797 0.707 1.504	0.798 0.707 1.506	0.799 0.708 1.507	0.800 0.709 1.509	0.801 0.710 1.511
36	Dry Material Water Slurry	0.771 0.711 1.482	0.772 0.712 1.484	0.772 0.713 1.485	0.773 0.714 1.487	0.774 0.714 1.488	0.775 0.715 1.490	0.776 0.716 1.492	0.777 0.717 1.493	0.778 0.717 1.494	0.779 0.718 1.496
		0.749 0.719 1.468	0.750 0.720 1.470	0.750 0.721 1.471	0.751 0.722 1.473	0.752 0.722 1.474	0.753 0.723 1.476	0.753 0.724 1.477	0.754 0.725 1.479	0.755 0.725 1.480	0.756 0.726 1.482
		0.727 0.728 1.455	0.728 0.728 1.456	0.729 0.729 1.458	0.730 0.729 1.459	0.730 0.731 1.461	0.731 0.731 1.462	0.732 0.732 1.464	0.732 0.733 1.465	0.733 0.733 1.466	0.734 0.734 1.468
37	Dry Material Water Slurry	0.727 0.728 1.455	0.728 0.728 1.456	0.729 0.729 1.458	0.730 0.729 1.459	0.731 0.731 1.461	0.731 0.732 1.462	0.732 0.732 1.464	0.732 0.733 1.465	0.733 0.733 1.466	0.734 0.734 1.468
		0.727 0.728 1.455	0.728 0.728 1.456	0.729 0.729 1.458	0.730 0.729 1.459	0.731 0.731 1.461	0.731 0.732 1.462	0.732 0.732 1.464	0.732 0.733 1.465	0.733 0.733 1.466	0.734 0.734 1.468
		0.727 0.728 1.455	0.728 0.728 1.456	0.729 0.729 1.458	0.730 0.729 1.459	0.731 0.731 1.461	0.731 0.732 1.462	0.732 0.732 1.464	0.732 0.733 1.465	0.733 0.733 1.466	0.734 0.734 1.468

Density of water at 30 deg. C. $d = 0.9957$ gr. per c.c.

$$\text{Density of dry raw material} = \frac{0.9957}{1 - \frac{(90.3442 - 67.0957)}{(73.4633 - 17.6455) (1 - \frac{34.18}{100})}}$$

$$= 2.712 \text{ gr. per c.c.}$$

The various types of raw material used in cement manufacture might be expected to show substantially different densities. Although the individual components of a mix vary in density, the values for the final kiln feed seem to vary only within a comparatively narrow range, even with diverse types of raw materials from widely separated localities.

TABLE II.—PRESSURE OF SLURRY IN LB. PER SQUARE INCH PER FOOT OF HEAD OF SLURRY.

Temperature: 30 degrees C. Raw-Material Density: 2.73 grams per cc.

Moisture in Slurry (%)	Pressure (pounds per square inch per 1 foot of head)
30	0.777
31	0.769
32	0.760
33	0.752
34	0.743
35	0.735
36	0.727
37	0.720
38	0.712
39	0.705
40	0.698
41	0.691
42	0.684
43	0.677
44	0.670
45	0.664
46	0.657
47	0.651
48	0.645
49	0.639
50	0.633

The average results for ten different raw materials are in gr. per c.c.: 2.746, 2.730, 2.758, 2.704, 2.740, 2.729, 2.721, 2.712, 2.732, 2.746, 2.732. In the absence of definite knowledge a value of 2.73 gr. per c.c. may be assumed with little possibility of serious error. However, for accurate work the value should be actually determined.

Table I gives the component weights of 1 c.c. of slurry at 30 deg. C. for densities of the dry raw material ranging from 2.7 to 2.8 gr. per c.c., and for moisture contents from 30 to 50 per cent. For example, with a raw-material density of 2.75 gr. per c.c. and 36 per cent. moisture, slurry is made up (in grammes per c.c. of slurry) of raw material, 1.077; water, 0.606; total, 1.683. The first figure, showing grammes of raw material per c.c. of slurry, if multiplied by the factors in Table II, gives barrels of clinker per cubic foot of slurry for various weights of dry raw material per barrel.

Table II gives the static pressure per 1 ft. head of slurry at various moisture contents. It also is based on a raw-material density of 2.73 gr. per c.c.